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EU MSCA-ETN DEMETER

Sm/Co separation by solvent extraction with ionic liquids

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Promoter: Prof. Dr. Koen Binnemans
Co-promoter: Dr. Tom Vander Hoogerstraete

Sm/Co separation by solvent extraction with ionic liquids:

SmCo magnets

- Method

  Solvent extraction with ionic liquids

- Results

  Three solvent extraction systems were compared:

  [A336][SCN]
  [A336][Cl]
  [A336][NO_3]

  } from chloride aqueous media

- Next steps in my research plan

A336 = ionic liquid Aliquat® 336

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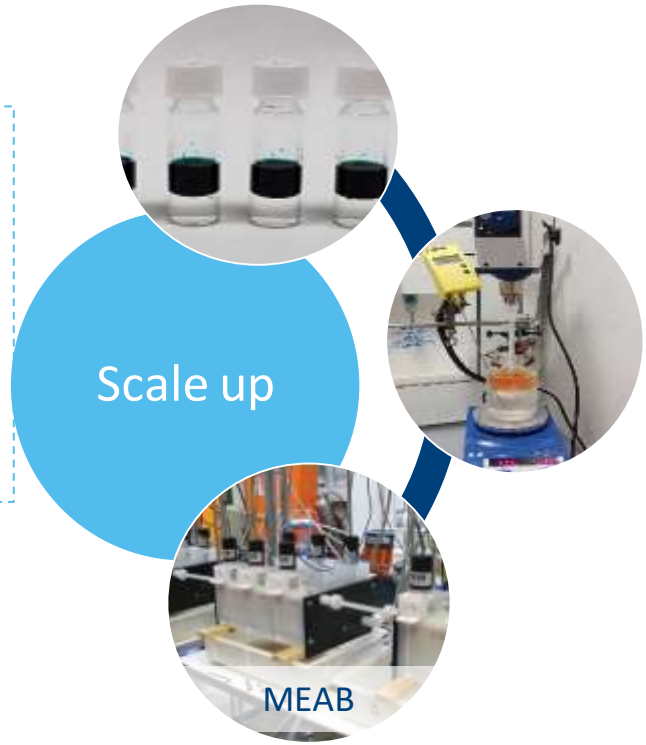
My goals

SmCo magnets:

1. Solvent extraction with undiluted ionic liquids.

2. Scale up to the continuous process (mixer-settler).



TARGET: To reach a high purities of recovered metal oxides: REEs (≥ 99.5%) and Co (≥ 99.0%).

REEs = rare-earth elements

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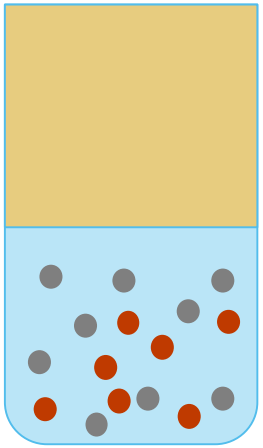
Method

Solvent extraction:

ORGANIC PHASE

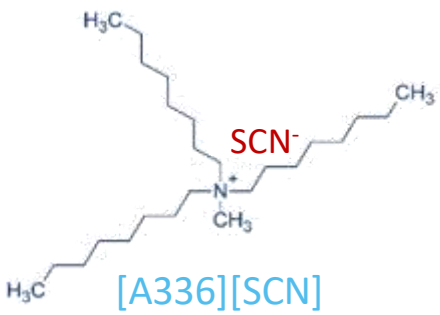
↓ density liquid



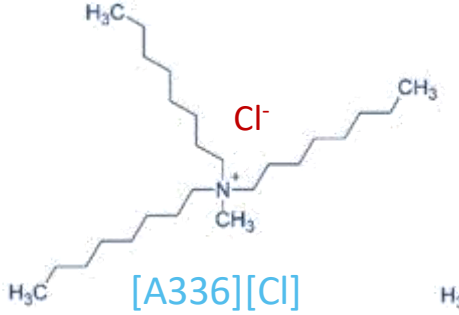
AQUEOUS PHASE

↑ density liquid

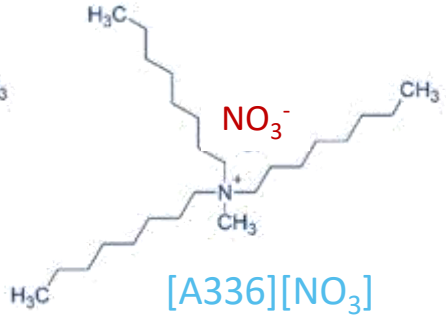
Organic phase = IONIC LIQUID



[A336][SCN]



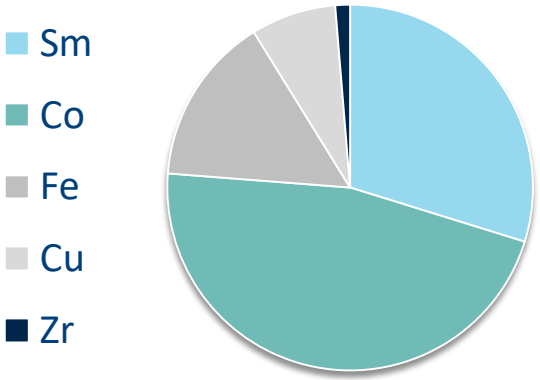
[A336][Cl]



[A336][NO_3]

Aqueous phase = ↑ conc. CHLORIDE SOLUTION

SmCo magnets:



Synthetic metal solution:

		c [g/L]
REE	Sm	95
transition metals	Co	98
	Cu	8

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Ionic liquids in solvent extraction

Ionic liquids are organic salts, which consist entirely of ions.

- Non-volatile or very low-volatile.
- Can be used undiluted.
- Non-flammable.
- No risks of electrostatic ignition.
- Safer work environment.

- Higher viscosity.
- Elevated temperatures lower the viscosity !

Extraction experiments

Conditions:	O/A = 1, 40 °C, 2 000 rpm, 2 h
	(Turbo Thermo Shakers TMS-200).
Metal analysis:	Total Reflection X-ray Fluorescence (TXRF).

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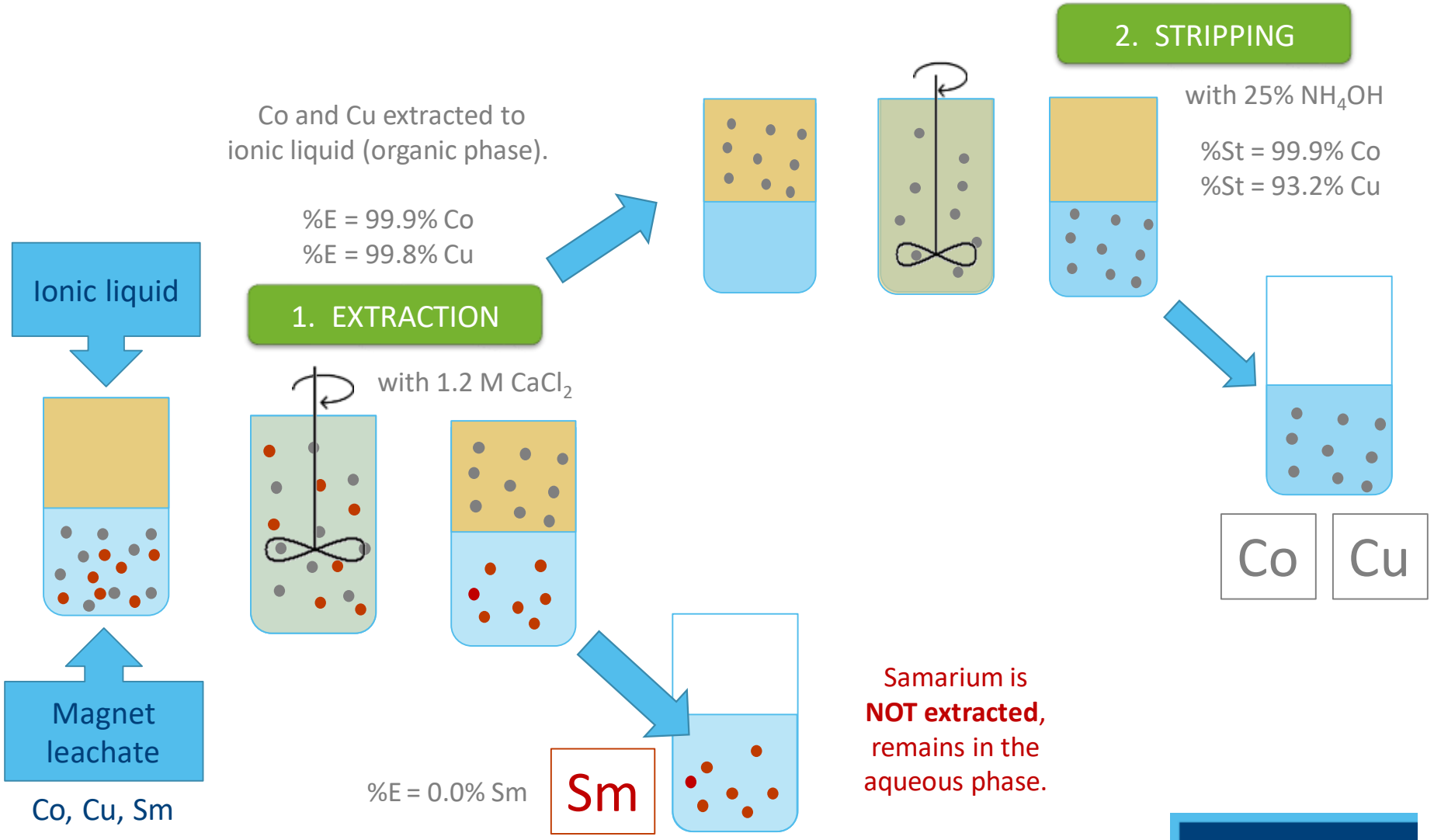
System [A336][SCN]



System [A336][SCN]

Problems related to thiocyanate

[A336][SCN]
stability

The precipitation stripping with NH_4OH leads to errors in measuring the metal concentrations, insoluble metal hydroxides are formed.

▼ Formation of precipitates.

Thiocyanate is not stable in the presence of strong acids/basis, elevated temperatures and is photosensitive [1], [2].

◄ Fresh (left) and 5 months old (right) solution of NH_4SCN.

[1] **Acidic aqueous decomposition of thiocyanogen**
Jon J. Barnett, Michael L. McKee, David M. Stanbury, *Inorganic Chemistry* ***43*** (16), 5021-5033 (2004).

[2] **Studien über das freie Rhodan**
E. E. Soderback, *Justus Liebigs Ann. Chem* **419**, 217–321 (1919).

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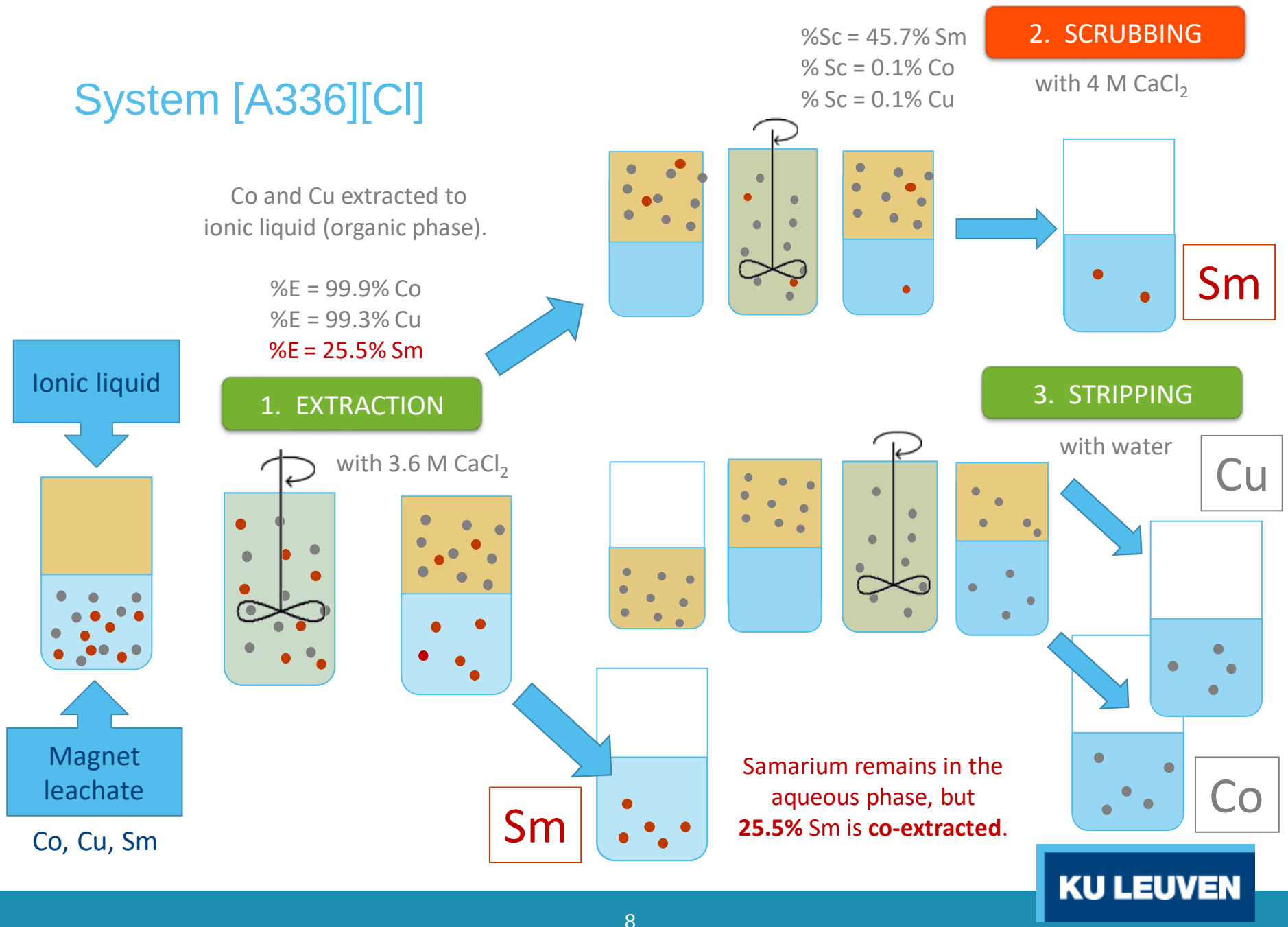
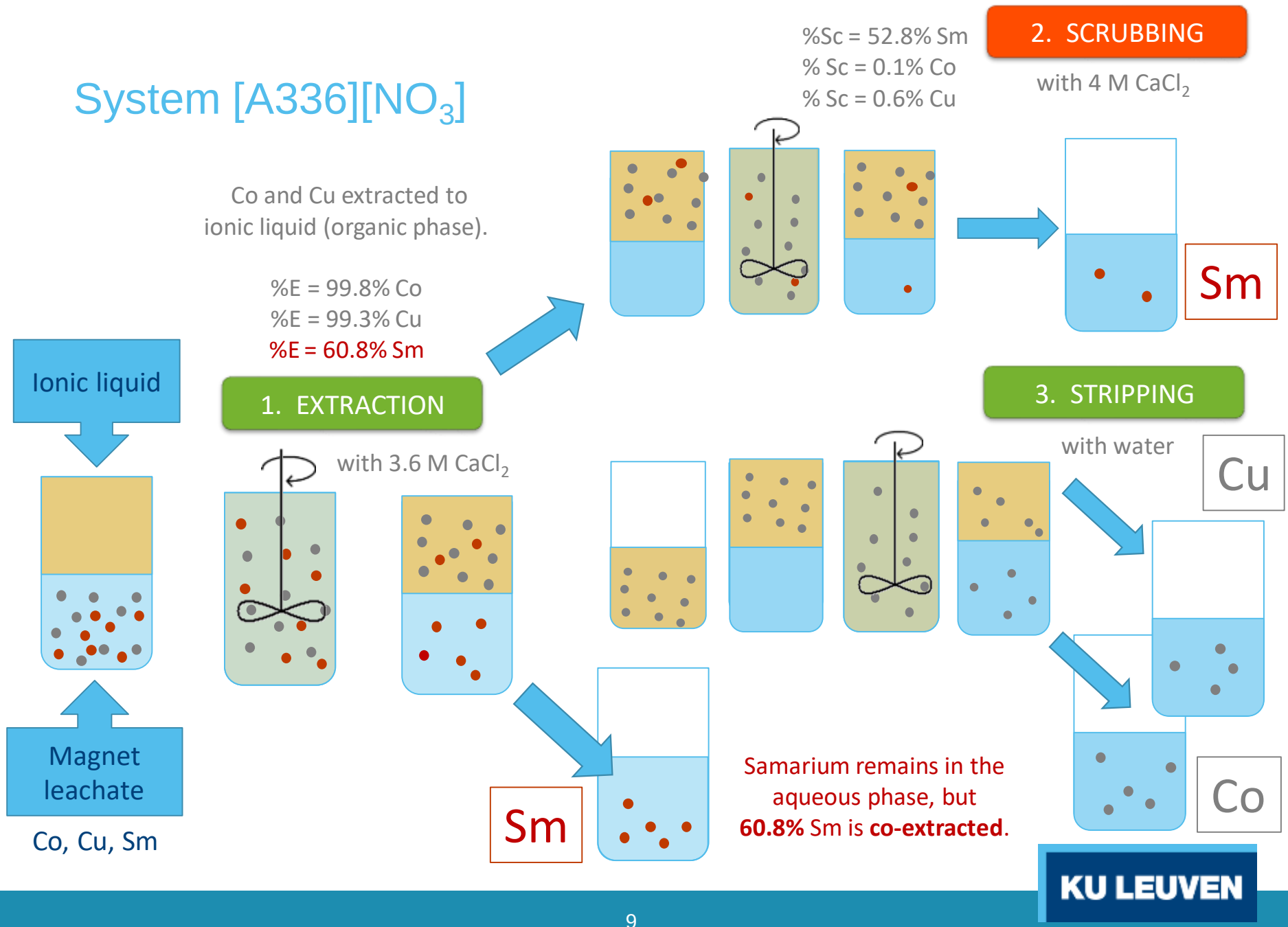
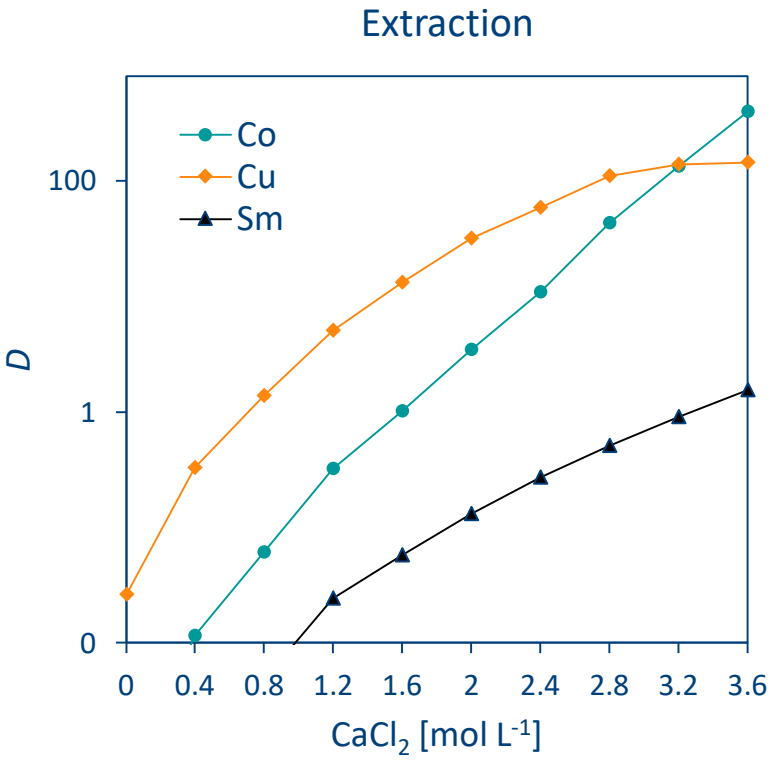
System [A336][Cl]

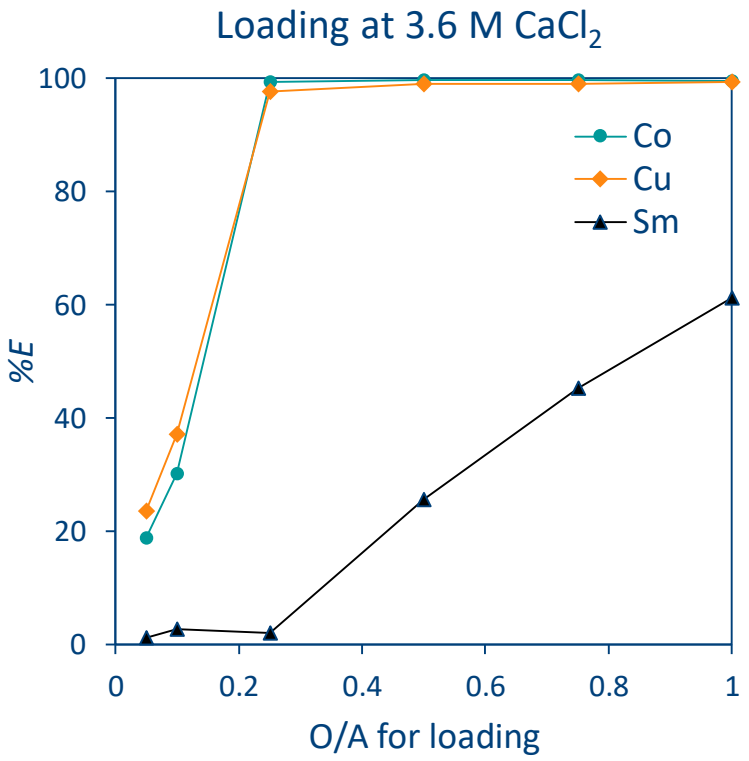


System [A336][NO_3]



System [A336][NO_3]





Distribution ratio: $D_{Me} = \frac{[Me]_{IL}}{[Me]_{aq}}$

Extraction efficiency: $\%E_{Me} = \frac{[Me]_{IL}}{[Me]_{aq} + [Me]_{IL}} \; x \; 100$

Structure of the formed complexes

Extraction with single metal solution:

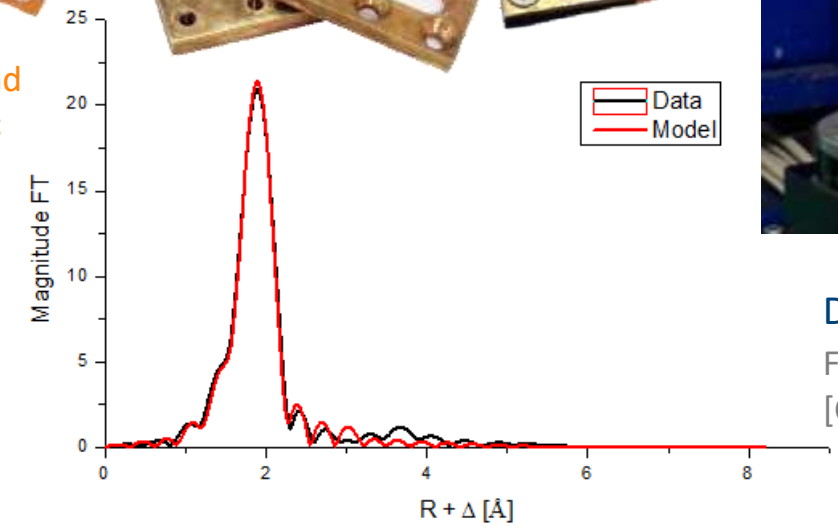
Co

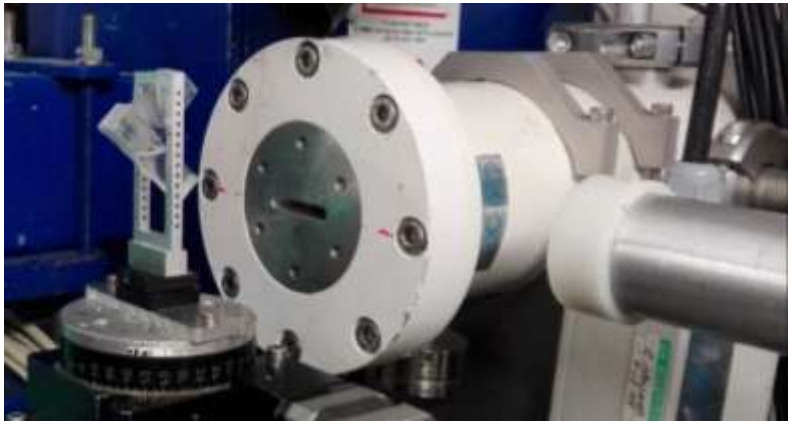
Extended X-ray Absorption Fine Structure spectroscopy (EXAFS).

The Dutch-Belgian Beamline (DUBBLE, BM26A) at the European Synchrotron Radiation Facility in Grenoble (France):

Kapton® windows and a flexible polymeric spacer VITON®

Brass holders





Data modeling in the program Viper:

Fourier transform and model of the $[CoCl_4]^{2-}$ complex in [A336][Cl].

Summary of results

Extraction system	Extraction results		Complexes formed		Associated problem
	Not extracted	Extracted	REE	Transition metals	
[A336][SCN] from chloride media at 1.2 M $CaCl_2$	100% Sm	Co, Cu *	$[Sm(SCN)_8]^{5-}$	$[Co(SCN)_4]^{2-}$ $[Cu(SCN)_4]^{2-}$	[A336][SCN] stability
[A336][Cl] from chloride media at 3.6 M $CaCl_2$	~ 75% Sm	Co, Cu ~ 25% Sm co-extracted	$[Sm(H_2O)_9]^{3+}$	$[CoCl_4]^{2-}$ $[CuCl_4]^{2-}$	[A336][Cl] selectivity
[A336][NO_3] from chloride media at 3.6 M $CaCl_2$	~ 40% Sm	Co, Cu ~ 60% Sm co-extracted	$[Sm(NO_3)_5]^{2-}$	$[CoCl_4]^{2-}$ $[CuCl_4]^{2-}$	[A336][NO_3] selectivity

* Co and Cu are preferentially extracted before Sm.

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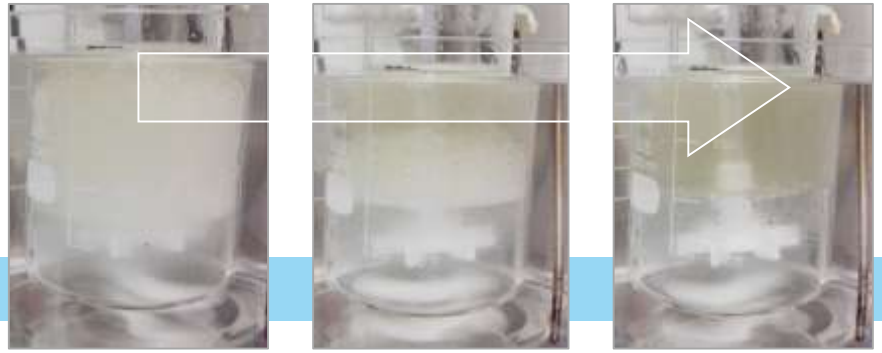
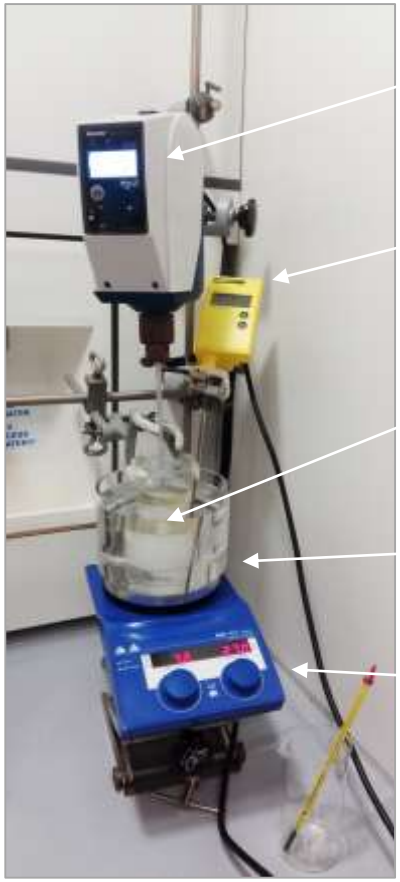
Phase disengagement





overhead stirrer
(WiseStir® HS-30D)

contact thermometer
(IKA® Yellow Line TC1)

250 mL beaker

silicon oil bath

heating plate
(IKA® RCT Basic)

O/A = 1,
2 min stirring

SETTLING TIME

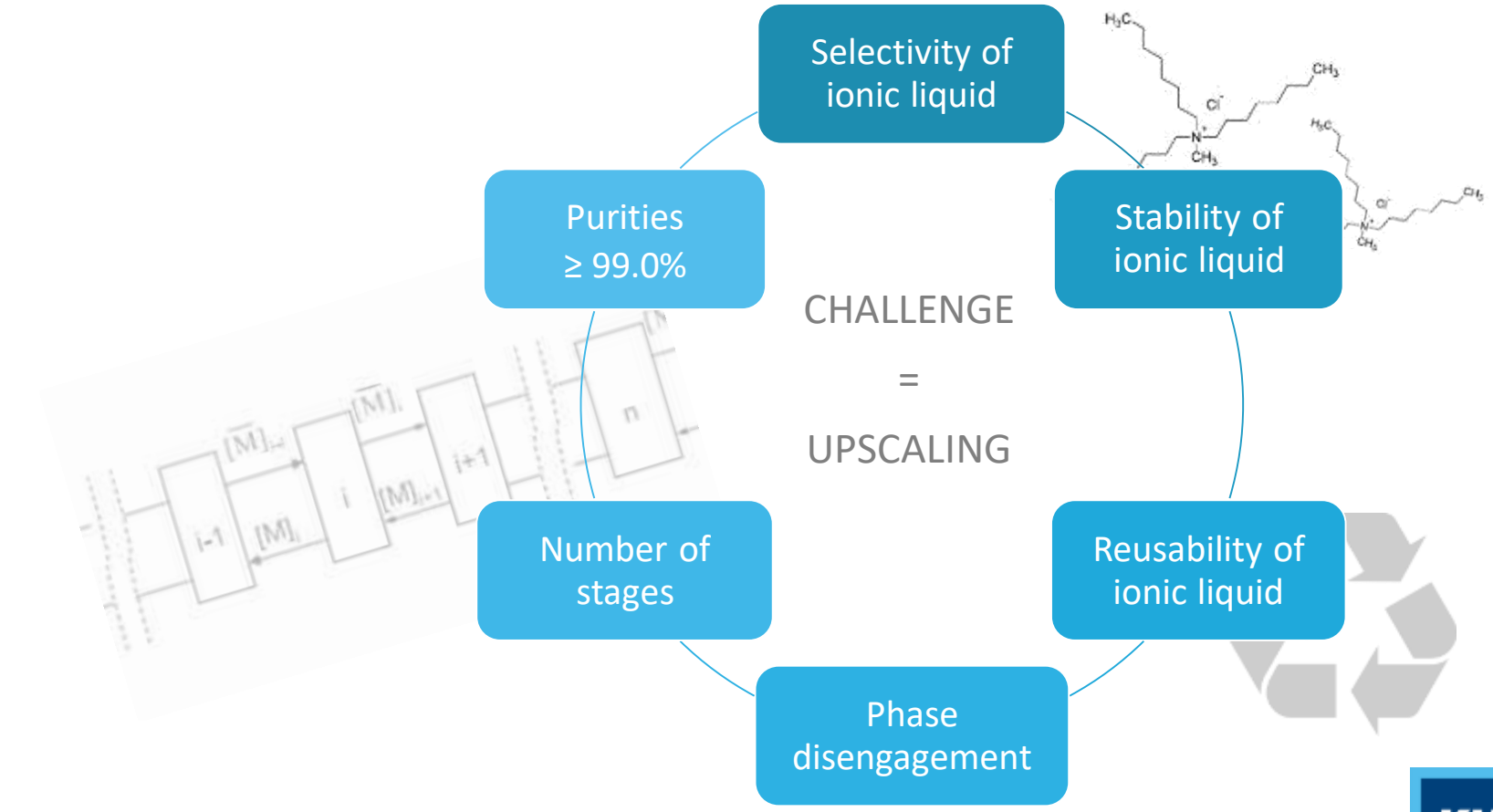
Addition of salt (0, 1, 2, 4 M $CaCl_2$).
Stirring speed (200, 300, … 700 rpm).
Temperature (22, 32, … 82 °C).
Position of stirrer (aqueous / organic phase).
Kind of stirrer:

Next steps in my research plan

2. Scale up to the continuous process (mixer-settler).

What is innovative:

- Using undiluted ionic liquids.
- Solvent extraction as a continuous process for SmCo magnets recycling.



Acknowledgements

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Co-promoter: Dr. Tom Vander Hoogerstraete

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Project website: http://etn-demeter.eu/.

Thank you for your attention!

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